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DATE: December 18, 2001

U.S. APPLN. NO.  
(IF KNOWN, SEE 37 C.F.R. 1.5)

10/018215

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| INTERNATIONAL APPLICATION NO.<br>PCT/JP00/04179 | INTERNATIONAL FILING DATE<br>June 26, 2000 | PRIORITY DATE CLAIMED<br>June 25, 1999 |
|---|--|--|

## TITLE OF INVENTION: PROCESS FOR ELECTROLYTICALLY COLORING ALUMINUM MATERIAL

APPLICANT(S) FOR DO/EO/US: Ken EBIHARA; Daisuke NAGASAWA

1.  This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.  
(THE BASIC FILING FEE IS ATTACHED)
2.  This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3.  This express request to begin national examination procedures [35 U.S.C. 371(f)] at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4.  A proper demand for International Preliminary Amendment was made by the 19th month from the earliest claimed priority date.
5.  A copy of the International Application as filed [35 U.S.C. 371(c)(2)]
  - a.  is transmitted herewith (required only if not transmitted by the International Bureau).
  - b.  has been transmitted by the International Bureau.
  - c.  is not required, as the application was filed in the United States Receiving Office (RO/US).
6.  A translation of the International Application into English [35 U.S.C. 371(c)(2)].
7.  Amendments to the claims of the International Application under PCT Article 19 [35 U.S.C. 371(c)(3)]
  - a.  are transmitted herewith (required only if not transmitted by the International Bureau).
  - b.  have been transmitted by the International Bureau.
  - c.  have not been made; however, the time limit for making such amendments has NOT expired.
  - d.  have not been made and will not be made.
8.  A translation of the amendments to the claims under PCT Article 19 [35 U.S.C. 371(c)(3)].
9.  An oath or declaration of the inventor(s) [35 U.S.C. 371(c)(4)].
10.  A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 [35 U.S.C. 371(c)(5)].

Items 11 - 16 below concern other document(s) or information included:

11.  An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98.
12.  An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. 3.28 and 3.31 is included.
13.  A **FIRST** preliminary amendment.  
 A **SECOND** or **SUBSEQUENT** preliminary amendment.
14.  A substitute specification.
15.  A change of power of attorney and/or address letter.
16.  Other items or information:  
Drawings (1 sheet)  
International Search Report  
Notification of Receipt of Record Copy (PCT/IB/301)  
Notification Concerning Submission of Priority Documents (PCT/IB/304)  
Notice Informing the Applicant of the Communication of the International Application to the Designated Offices (PCT/IB/308)  
Information Concerning Elected Offices Notified of Their Election (PCT/IB/332)  
Front Page of International Bulletin No. WO 01/00904 A1

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|---|--------------|---|---|
| U.S. APPN NO (IF KNOWN)<br>SEE 37 C.F.R. 1.50)<br><b>10/018215</b>  |              | INTERNATIONAL APPLICATION<br>NO. PCT/JP00/04179 | ATTORNEY DOCKET NO. NAN-0201<br><br>DATE: December 18, 2001 |
| <p>17. <input type="checkbox"/> The following fees are submitted:</p> <p><b>Basic National Fee [37 C.F.R. 1.492(a)(1)-(5)]:</b><br/>           Search Report has been prepared by the EPO or JPO.....\$890.00<br/>           International preliminary examination fee paid to USPTO<br/>           (37 C.F.R. 1.482).....\$710.00<br/>           No international preliminary examination fee paid to USPTO<br/>           (37 C.F.R. 1.482) but international search fee paid to USPTO<br/>           [37 C.F.R. 1.445(a)(2)].....\$740.00<br/>           Neither international preliminary examination fee<br/>           (37 C.F.R. 1.482) or international search fee<br/>           [37 C.F.R. 1.445(a)(2)] paid to USPTO.....\$1,040.00<br/>           International preliminary examination fee paid to USPTO<br/>           (37 C.F.R. 1.482) and all claims satisfied provisions of<br/>           PCT Article 33(2)-(4).....\$ 100.00         </p> |              | CALCULATIONS                                    | PTO USE ONLY  |
| <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>   |              | \$ 890.00                                       |   |
| Surcharge of \$130.00 for furnishing the oath or declaration later<br>than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date<br>[37 C.F.R. 1.492(e)].  |              | \$  |   |
| Claims  | Number Filed | Number Extra                                    | Rate  |
| Total Claims  | 8 - 20 =     | 0   | X \$ 18.00  |
| Independent Claims  | 1 - 3 =      | 0   | X \$ 84.00  |
| Multiple dependent claim(s) (if applicable)   |              | + \$280.00                                      | \$ 280.00   |
| <b>TOTAL OF ABOVE CALCULATIONS =</b>  |              | \$ 1170.00                                      |   |
| Reduction by one-half for filing by small entity, if applicable.<br>Verified Small Entity statement must also be filed.<br>(Note 37 C.F.R. 1.9, 1.27, 1.28).  |              | \$  |   |
| <b>SUBTOTAL =</b>   |              | \$ 1170.00                                      |   |
| Processing fee of \$130.00 for furnishing the English translation<br>later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date<br>[37 C.F.R. 1.492(f)]. +  |              | \$  |   |
| <b>TOTAL NATIONAL FEE =</b>   |              | \$ 1170.00                                      |   |
| Fee for recording the enclosed assignment [37 C.F.R. 1.21(h)]. The assignment<br>must be accompanied by an appropriate cover sheet<br>(37 C.F.R. 3.28, 3.31). \$40.00 per property +  |              | \$  |   |
| <b>TOTAL FEES ENCLOSED =</b>  |              | \$ 1170.00                                      |   |
|   |              | Amount to be refunded                           | \$  |
|   |              | Charged   | \$ 1170.00  |
| a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.   |              |   |   |
| b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 18-0013 in the amount of \$1170.00 to cover the above fee.<br>A duplicate copy of this sheet is enclosed.   |              |   |   |
| c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to<br>Deposit Account No. 18-0013.  |              |   |   |
| NOTE: Where an appropriate time limit under 37 C.F.R. 1.494 or 1.495 has not been met, a petition to revive<br>[37 C.F.R. 1.137(a) or (b)] must be filed and granted to restore the application to pending status.  |              |   |   |
| SEND ALL CORRESPONDENCE TO:<br><b>Customer No. 23353</b>  |              |   |   |
| Rader, Fishman & Grauer PLLC<br>1233 20 <sup>th</sup> Street, N.W.,<br>Suite 501<br>Washington, D.C. 20036<br>Tel: (202) 995-3750 Fax: (202) 995-3751   |              |   |   |
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## S P E C I F I C A T I O N

### Title of the Invention

Process For Electrolytically Coloring Aluminum Material

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### Field of Technology

This invention relates to a process for electrolytically coloring an aluminum material consisting of anodized aluminum or an anodized aluminum alloy (hereinafter simply referred to as "aluminum material"); more particularly, this invention relates to a process for electrolytically coloring an aluminum material which can attain uniformity in color tone during alternating current electrolytic coloring and, still more, to a process for electrolytically coloring an aluminum material which can keep the color tone from changing irregularly not only in a given energizing lot but also in different energizing lots during electrolytic coloring thereby producing an aluminum material colored in a uniform tone.

### Background Technology

An aluminum material is used frequently in many areas such as construction materials, vehicle parts and furniture on account of its good processability and corrosion resistance and, for the purpose of enhancing the aesthetic effect of the material, electrolytic coloring has been practiced wherein an aluminum material is subjected to electrolysis in an electrolyte containing a

soluble salt of metal such as Ni, Co, Cu, and Sn thereby causing the electrolysis product of the metal salt to deposit in the porous anodic oxide film.

The following processes are known for electrolytic coloring of an aluminum material; alternating current electrolytic coloring (Asada process) wherein an alternating current is passed through an electrolyte to effect electrolysis and direct current electrolytic coloring wherein a direct current is passed through an electrolyte. Each process has its own advantages and the former can utilize a low-cost power source to reduce the equipment cost while the latter can perform electrolytic coloring in a relatively short time and, in particular, is known to attain sufficiently uniform coloring in the case of electrolytic coloring in dark tone such as black.

A problem arises, however, in the aforementioned electrolytic coloring of an aluminum material, particularly in the cases in which an aluminum material has a complicated shape or aluminum materials of various shapes are treated simultaneously; irregular coloring tends to occur in the depressed and projected parts, the color tone lacks uniformity and deviates from the range approved by clients, the product yield drops and, as a result, the product cost runs up.

Such being the case, a variety of processes have been proposed to solve this problem. For example, one of them performs a pretreatment of an aluminum material prior to alternating current electrolytic coloring by passing a direct current in the same electrolytic coloring bath with the aluminum material used as the anode; constant voltage electrolysis is known as such wherein a

direct current is passed for a given length of time while maintaining the voltage at a constant value [Japan Tokkyo Koho Sho 54-23,664 (1979)].

This pretreatment prior to coloring by constant voltage electrolysis aims at eliminating irregular coloring by passing a direct current at constant voltage for a certain length of time thereby making the resistance of the anodic oxide film uniform in various parts and creating a condition for a relatively uniform current to flow through the oxide film during alternating current electrolytic coloring which follows the pretreatment; this process is commercially admissible in the cases in which an aluminum material is electrolytically colored in a relatively dark tone.

Another process proposes the following procedure for electrolytic coloring of an aluminum material; a stable color tone is attained by repeating passage and stoppage of electric current in multiple stages intermittently and meanwhile setting the voltage successively higher from one stage to the subsequent stage [Japan Kokai Tokkyo Koho Hei 8-41,685 (1996)]. It is said that the process undoubtedly attains a stable color tone and additionally shortens the time required for coloring in black, and controls the influence of trace amounts of impurities thereby preventing white streak defects.

Any of the aforementioned processes can attain a relatively stable color tone in a given energizing lot, but is unable to control irregularities in color tone in different energizing lots completely and, in consequence, produces with difficulty an aluminum material colored in a uniform tone in different energizing lots.

This tendency to irregularity does not matter very much in electrolytic coloring in a relatively dark tone, but becomes pronounced in electrolytic coloring in a relatively light tone and poses a problem in commercial production of an electrolytically colored aluminum material.

Another process proposed to solve the aforementioned problem is alternating current electrolytic coloring which is effected by changing the total current density that is the sum total of the absolute values of positive and negative current densities of the current waveform stepwise from the first step to at least the fourth step [Japan Tokkyo Koho Hei 3-32,637 (1991)]. This process can somehow manage to do as much as keeping the difference in color tone from becoming real in the case of electrolytic coloring of an aluminum material in a relatively light tone.

This process, however, faces another problem in that the control of current becomes extremely complicated and the equipment cost goes up to its economical disadvantage. Moreover, in electrolytic coloring of an aluminum material in a relatively light tone such as bronze, a slight difference in color tone becomes emphasized and conspicuous depending upon the condition of light and greatly affects the value of commodities. A case of this kind presents a big problem in commerical production of an electrolytically colored aluminum material.

Under these circumstances, the present inventors have conducted studies to develop a process for producing an aluminum material colored in a uniform tone stably and commercially advantageously while preventing irregular

coloring in different energizing lots as much as possible in alternating current electrolytic coloring and found that a uniform color tone can be attained in different energizing lots even in electrolytic coloring in a relatively light tone by performing a pretreatment prior to coloring that precedes alternating current electrolytic coloring until the voltage and current respectively reach the preset ultimate values.

According to the literature survey and research works of the present inventors, irregularity in color tone in different energizing lots in alternating current electrolytic coloring of an aluminum material seems to occur for the following reasons.

For example, in case a pretreatment prior to coloring is performed by constant current electrolysis in the same electrolytic coloring bath as used for alternating current electrolytic coloring of an aluminum material, the bath voltage in the pretreatment prior to coloring is affected by the temperature and pH of the electrolytic coloring bath and, still more, by the water washing time and the pH of the water washing bath during the step for water washing of the anodized aluminum material before immersion in the electrolytic coloring bath (the aforementioned conditions are hereinafter collectively referred to as "the bath conditions") and the bath voltage changes with the bath conditions.

Now, the bath voltage in the pretreatment prior to coloring by constant current electrolysis is decided primarily by the resistance of the electrolytic coloring bath and the resistance of the anodic oxide film on the surface of

aluminum material immersed in the bath. As changes in the resistance of the electrolytic coloring bath from energizing lot to energizing lot are not very large, at most 0.1-0.2 V in terms of the corresponding voltage, changes in the bath voltage in the pretreatment prior to coloring are considered to be due chiefly to the resistance of the anodic oxide film. The anodic oxide film on the surface of aluminum material consists of the so-called "barrier layer" which is a fine aluminous layer formed on the aluminum substrate of an aluminum material and a porous layer formed on the barrier layer and the resistance of the anodic oxide film is practically that of the barrier layer.

The efficiency for formation of the barrier layer in the pretreatment prior to coloring by constant current electrolysis is considered to be 60% or so in terms of apparent efficiency that is the ratio of the theoretical amount formed with the current efficiency assumed to be 100% to the actual amount increased with the dissolution of the barrier layer taken into account (amount increased/theoretical amount formed). Moreover, since the rate of chemical dissolution of the barrier layer is affected by changes in the bath conditions, the apparent efficiency changes under the influence of the bath conditions like the aforementioned bath voltage in the pretreatment prior to coloring; as a result, the resistance of the anodic oxide film on the surface of aluminum material changes from energizing lot to energizing lot.

On the other hand, in the pretreatment prior to coloring by the conventional constant current electrolysis which is effected by passing a direct current at a constant value for a given length of time, the bath voltage changed

in a given energizing period under the influence of "the changes in the bath voltage in the pretreatment prior to coloring" and "the changes in the resistance of the anodic oxide film on the surface of aluminum material" caused by the changes in the aforementioned bath conditions; as a result, it was not possible to control completely the formation of the barrier layer on the surface of aluminum material and to keep the current distribution in the anodic oxide film of aluminum material constant.

In order to obtain a uniform color tone in different energizing lots, a conceivable approach is to control the aforementioned bath conditions strictly and eliminate their influence. In reality, however, strict control of the bath conditions is difficult to perform on a commercial scale and changes of the bath conditions are unavoidable within the range of control and, in particular, it is impossible to suppress completely the unevenness in color tone in different energizing lots in the case of electrolytic coloring in a relatively light tone.

The present inventors have conducted studies to find a commercially adequate solution to the aforementioned problem, found that the thickness of the barrier layer of the anodic oxide film to be formed and adjusted in the pretreatment prior to coloring is dependent on the ultimate voltage and current to be reached finally in the pretreatment, for example, the thickness in question is proportional to the ultimate voltage in the case of the pretreatment prior to coloring by constant current electrolysis, and, as a result, the thickness of the barrier layer is directly related to the color tone given to the aluminum material by alternating current electrolytic coloring, and completed this

invention.

Accordingly, an object of this invention is to provide a process for electrolytically coloring an aluminum material which is capable of preventing as much as possible irregularities in coloring not only in a given energizing lot but also in different energizing lots in alternating current electrolytic coloring of an aluminum material and producing an aluminum material colored in a uniform tone stably and easily on a commercial scale.

#### Disclosure of the Invention

In a process for electrolytically coloring an aluminum material which comprises immersing an aluminum material consisting of anodized aluminum or an anodized aluminum alloy in an electrolytic coloring bath containing a soluble metal salt, performing a pretreatment prior to coloring by passing a direct current waveform with the aluminum material serving as the anode, and performing alternating current electrolytic coloring in the same electrolytic coloring bath, this invention relates to an improved process for electrolytically coloring an aluminum material which comprises performing said pretreatment prior to coloring until the voltage and current respectively reach the preset ultimate voltage and current.

In this invention, a particularly desirable mode of execution of the process for electrolytically coloring an aluminum material comprises performing a pretreatment prior to coloring by constant current electrolysis wherein a direct current is passed until the voltage reaches the ultimate value while

maintaining the current at the preset ultimate value and then performing alternating current electrolytic coloring wherein a voltage-controlled alternating current waveform that has the peak voltage 0.55-0.8 times the final voltage in the pretreatment prior to coloring by constant current electrolysis is passed through the aluminum material.

There is no specific restriction on an aluminum material to be electrolytically colored in this invention and, as in the conventional anodizing, a direct current, an alternating current, or an alternating current superimposed on a direct current is passed through an electrolytic bath containing an aqueous solution of acid such as sulfuric acid, oxalic acid, sulfonic acid, and chromic acid with an aluminum raw material consisting of ordinary aluminum or an aluminum alloy serving as the anode to form an anodic oxide film on the surface of the aluminum raw material.

There is also no specific restriction on the electrolytic coloring bath containing a soluble metal salt intended for the pretreatment prior to coloring and for alternating current electrolytic coloring of the aluminum material obtained in the aforementioned manner and any electrolytic coloring bath similar to the conventional one is acceptable. Soluble metal salts include inorganic salts such as sulfates, nitrates, phosphates, chlorides, and chromates and organic salts such as oxalates, acetates, and tartrates of metals such as nickel (Ni), cobalt (Co), copper (Cu), tin (Sn), chromium (Cr), magnesium (Mg), iron (Fe), cadmium (Cd), titanium (Ti), manganese (Mn), molybdenum (Mo), calcium (Ca), vanadium (V), lead (Pb), and zinc (Zn).

For the purpose of improving the degree of coloring, it is allowable, if necessary, to add the following compounds including strong reducing agents as additives to the electrolytic coloring bath: dithionites such as sodium dithionite and zinc dithionite, thiosulfates such as ammonium thiosulfate and sodium thiosulfate, hydrogen sulfites such as sodium hydrogen sulfite, sulfurous acid, sulfites such as sodium sulfite, thioglycolic acid, and thioglycolates such as ammonium thioglycolate.

The pretreatment prior to coloring preceding alternating current electrolytic coloring in this invention is performed by immersing an aluminum material in the electrolytic coloring bath, passing a direct current waveform (that is, direct current or an alternating current superimposed on a direct current) with the aluminum material serving as the anode, and completing the operation at the point when the voltage (the peak voltage in case the direct current waveform is that of an alternating current superimposed on a direct current) and the current respectively reach the preset ultimate values.

In performing the pretreatment prior to coloring, for example, by constant current electrolysis which is effected by passing a current of a constant value, a concrete procedure is to pass a direct current while keeping the current at the preset value of ultimate current and terminate the pretreatment when the voltage reaches the preset value of ultimate voltage. In the initial stage of this constant current pretreatment, the current flows preferentially to the portion where the barrier layer of the anodic oxide film on the surface of aluminum material is relatively thin and offers a low resistance and to the portion near

the cathode where the resistance of the bath is low; the barrier layers either get compensated for small thickness or grow relatively thicker by the amount corresponding to the difference in resistance of the bath in these portions and a constant anodic current distribution is obtained when the voltage reaches the ultimate value.

On the other hand, in case the pretreatment prior to coloring is performed by constant voltage electrolysis by passing a current at constant voltage, there is normally a danger of overcurrent if a current of the preset ultimate voltage is passed from the start in the initial stage. To prevent the flow of overcurrent, a direct current waveform is passed at a lower voltage than the preset ultimate voltage in the initial stage and, when the current stabilizes, the voltage is switched over to the ultimate voltage and the constant voltage electrolysis is continued until the current reaches the preset ultimate value.

Setting of the ultimate voltage and current in the pretreatment prior to coloring varies with what color tone is required for the aluminum material as product; the ultimate voltage is preferably set at 30-50 V for electrolytic coloring in a relatively light tone or at 20-30 V for electrolytic coloring in a relatively dark tone and the ultimate current is preferably set in the range 20-50 A/m<sup>2</sup>.

Upon completion of the pretreatment prior to coloring in this manner, this invention performs alternating current electrolytic coloring in the same electrolytic coloring bath by passing an alternating current waveform or a superimposed AC-DC waveform through the aluminum material.

In this case, there is no specific restriction on the procedure for alternating current electrolytic coloring and the conventional procedure can be adopted. For the reason given below, the peak voltage of the alternating current waveform or superimposed AC-DC waveform in use is set at a value preferably 0.55-0.8 times, more preferably 0.65-0.75 times, the value of the preset ultimate voltage in the pretreatment prior to coloring. If the peak voltage is lower than 0.55 times, coloring does not occur or the rate of coloring becomes extremely low. On the other hand, if the peak voltage exceeds 0.8 times, the current becomes difficult to stay constant in alternating current electrolytic coloring and a uniform color tone cannot be obtained even if the time for treatment is fixed.

This situation can be understood as follows according to the studies of the present inventors.

In electrolytic coloring, a metal species in the bath is reduced and deposited inside the oxide film to produce a color tone. Therefore, making the color tone uniform is nothing less than making the current distribution in the aluminum material uniform when electrolytic coloring is performed with the aluminum material serving as the anode.

In case the pretreatment prior to coloring is performed with the aluminum material as the anode by controlling the current and regulating the final voltage, the film resistance corresponding to the bath resistance in each part is generated and the current distribution of the aluminum material can be made constant and nearly uniform at the end of the pretreatment prior to coloring.

However, in case alternating current electrolytic coloring is performed thereafter by passing an alternating current waveform, the current distribution in the aluminum material becomes nonuniform and the color tone becomes nonuniform in spite of the fact that the current distribution in the aluminum material is nearly uniform at the end of the pretreatment prior to coloring if the peak voltage of the alternating current waveform is equal to or higher than the final voltage in the current-controlled pretreatment prior to coloring. This is because the film resistance itself has a property of varying with the direction of current and the resistance in the case of the aluminum material serving as the cathode is less than in the case of the aluminum material serving as the anode.

As a result of studies of this problem, the present inventors have found that the changes in film resistance in alternating current electrolytic coloring is dependent on and closely related to the ratio of the final voltage in the current-controlled pretreatment prior to coloring to the peak voltage of the alternating current waveform in alternating current electrolytic coloring. That is, the current-controlled pretreatment prior to coloring is performed first by passing a direct current while regulating the final voltage and then alternating current electrolytic coloring is performed in the same electrolytic coloring bath by passing a voltage-controlled alternating current waveform having the peak voltage 0.55-0.8 times the final voltage in the aforementioned current-controlled pretreatment prior to coloring and this procedure makes it possible to obtain a uniform current distribution corresponding to the changes in film

resistance at the end of the pretreatment prior to coloring and obtain a uniform color tone.

In actual operations, it is necessary for the purpose of improving productivity to select a voltage as high as possible within the range 0.55-0.8 times the final voltage. In order to satisfy the two requirements of uniform color tone and improved productivity, a preferable procedure is to scan the aluminum material pretreated and placed in the electrolytic coloring bath with alternating current voltage to plot a voltage-current curve, determine the boundary voltage  $E_0$  that is the intersection of the respective extension lines of the flat region and the rising region in the curve, and set the peak voltage in alternating current electrolytic coloring at this boundary voltage  $E_0$ . The boundary voltage  $E_0$  thus determined is normally 0.65-0.75 times the ultimate voltage preset in the current-controlled pretreatment prior to coloring and, although varying somewhat with the conditions for the pretreatment prior to coloring or other conditions (such as treatment of anodic oxide film and the subsequent water washing), it can be determined unambiguously as a suitable peak voltage of an alternating current waveform or a superimposed AC-DC waveform.

According to the process of this invention, an electric current flows with ease in the parts near the counter electrode in the initial and intermediate stages of the pretreatment prior to coloring and the barrier layer grows there preferentially. The film resistance increases as the barrier layer grows and the ease of flow of the current in this part is held in check. That is, preferential

growth of the barrier layer in the part where the current flows with ease in the pretreatment prior to coloring helps to eliminate the difference in site-dependent ease of current flow in alternating current electrolytic coloring thereby causing the current to flow with a nearly uniform current distribution over the whole surface of the aluminum material in a given energizing lot and eliminating irregularities in color tone in a given energizing lot.

Moreover, according to the process of this invention, the aforementioned pretreatment prior to coloring is performed until the voltage and current reach the preset ultimate values and, even if the bath conditions change in different energizing lots, the condition of the barrier layer finally adjusted by the pretreatment prior to coloring becomes constant in different energizing lots and the current flows with a nearly uniform current distribution over the whole surface of the aluminum material in different energizing lots and this eliminates irregularities in color tone in different energizing lots.

#### Brief Description of the Drawing

Fig. 1 is a voltage-current curve plotted in the determination of the boundary voltage  $E_0$  in Example 1.

#### Preferred Embodiments of the Invention

A preferable mode of execution of this invention will be described concretely with reference to test examples, examples, and comparative examples below.

##### [Example 1]

An aluminum raw material, A6063S-T5, was anodized in 20%  $H_2SO_4$  at a current density of  $100 \text{ A/m}^2$  for 30 minutes to form an anodic oxide film with a thickness of  $10 \mu\text{m}$  on the surface of the aluminum raw material and then washed in an acid bath at pH 1 for 5 minutes to prepare an aluminum material.

An electrolytic coloring bath composed of 25 g/l of  $CuSO_4$  and 5 g/l of  $H_2SO_4$  was prepared and the aforementioned aluminum material was submitted to the current-controlled pretreatment prior to coloring with the aluminum material serving as the anode at a current density of  $25 \text{ A/m}^2$ , a bath temperature of  $25^\circ\text{C}$ , and an ultimate voltage of 20 V for approximately 20 seconds.

Upon completion of the pretreatment in this manner, the pretreated aluminum material was scanned with alternating current voltage in the same coloring bath while raising the peak voltage from 0 V at a rate of 1 V/sec and a voltage-current curve was plotted.

The results are shown in Fig. 1 and the boundary voltage  $E_0$  was 14 V when the flat region and the rising region of the curve were respectively extended and the intersection of the two extension lines was read.

Alternating current electrolytic coloring was performed in the same coloring bath by setting the peak voltage of a commercial alternating current at this boundary voltage which is 14 V and passing the current for 50 seconds, 100 seconds, and 150 seconds to give the aluminum material electrolytically colored pink.

Color measurement was made on the electrolytically colored aluminum material thus obtained and the uniformity of color tone (color difference;  $\Delta E^*_{ab}$ ) in a given energizing lot was examined.

The treatment of the anodic oxide film, current-controlled pretreatment prior to coloring, and alternating current electrolytic coloring were repeated under the aforementioned conditions and the electrolytically colored aluminum material was submitted to color measurement to examine the uniformity of color tone (color difference;  $\Delta E^*_{ab}$ ) in different energizing lots. The results are shown in Table 1.

#### [Example 2]

The current-controlled pretreatment prior to coloring and alternating current electrolytic coloring were performed as in the aforementioned Example 1 except using the the conditions and the peak voltage of a commercial alternating current shown in Table 1 to give the electrolytically colored aluminum material.

The uniformity of color tone was examined as in Example 1 on the electrolytically colored aluminum material thus obtained. The results are shown in Table 1.

#### [Example 3]

Using the aluminum material prepared by anodizing the same raw material by the same method as in Example 1 and the same electrolytic coloring bath as in Example 1, the constant voltage pretreatment prior to coloring was

performed by placing the aluminum material as the anode, passing a direct current at a voltage of 15 V initially, switching the voltage over to 20 V thereafter at the point when the current density dropped to  $32 \text{ A/m}^2$ , and continuing the operation until the final current density became  $25 \text{ A/m}^2$ .

Upon completion of the constant voltage pretreatment prior to coloring, the material was scanned with commercial alternating current voltage in the same electrolytic coloring bath as in Example 1 and a voltage-current curve was plotted. The results are similar to those in Example 1 and the boundary voltage  $E_0$  determined from the intersection of the respective extension lines of the flat and rising region was 14 V.

Alternating current electrolytic coloring was performed in the same electrolytic coloring bath by setting the peak voltage of a commercial alternating current at this boundary voltage  $E_0$  of 14 V and passing the current for 100 seconds to give the aluminum material electrolytically colored pink.

The colored aluminum material was submitted to color measurement to examine the uniformity of color tone (color difference;  $\Delta E^{* ab}$ ) in a given energizing lot. The results are shown in Table 1.

#### [Comparative Example 1]

Alternating current electrolytic coloring was performed under the same conditions as in Example 1 without the current-controlled pretreatment prior to coloring and the electrolytically colored aluminum material thus obtained

was examined for the uniformity of color tone as in Example 1. The results are shown in Table 1.

[Comparative Examples 2 and 3]

The current-controlled pretreatment prior to coloring and alternating current electrolytic coloring were performed as in the aforementioned Example 1 except applying the peak voltage of a commercial alternating current shown in Table 1 and the electrolytically colored aluminum material thus obtained was examined for the uniformity of color tone as in Example 1. The results are shown in Table 1.

[Comparative Example 4]

The constant voltage pretreatment prior to coloring was performed at a bath voltage of 30 V for 30 seconds and alternating current electrolytic coloring was performed as in Example 2 and the electrolytically colored aluminum material thus obtained was examined for the uniformity of color as in Example 1. The results are shown in Table 1.

Table 1

|                     | Conditions for pretreatment prior to coloring     | Conditions for alternating current electrolytic coloring |                        |                                 | Color difference : $\Delta E^*_{ab}$ |                   |
|---------------------|---|--|------------------------|---------------------------------|--------------------------------------|-------------------|
|                     |   | Peak voltage<br>(*)1                                     | Voltage ratio<br>(**)2 | Time of energizing<br>: seconds | In a given lot                       | In different lots |
| Example             | Current-controlled pretreatment prior to coloring |  |                        | 50                              | 1                                    | $\leq 1$          |
|                     | 1 Current density : $25 \text{ A/m}^2$            | 14V  | 0.70                   | 100                             | 1                                    | $\leq 1$          |
|                     | Ultimate voltage : 20 V                           |  |                        | 150                             | 1                                    | $\leq 1$          |
|                     | Current-controlled pretreatment prior to coloring |  |                        | 50                              | 1                                    | $\leq 1$          |
|                     | 2 Current density : $50 \text{ A/m}^2$            | 21V  | 0.70                   | 100                             | 1                                    | $\leq 1$          |
|                     | Ultimate voltage : 30 V                           |  |                        | 150                             | 1                                    | $\leq 1$          |
| Comparative Example | Current controlled pretreatment prior to coloring |  |                        | 50                              |                                      |                   |
|                     | Voltage set initially : 15 V                      | 14V  | 0.70                   | 100                             | 2                                    | $\leq 2$          |
|                     | Voltage after switch-over : 20 V                  |  |                        | 150                             |                                      |                   |
|                     | Ultimate current density : $25 \text{ A/m}^2$     |  |                        |                                 |                                      |                   |
|                     | 1 No pretreatment prior to coloring               | 14V  | —                      | 50                              | $9^{(*)3}$                           | 5                 |
|                     | Current-controlled pretreatment prior to coloring |  |                        | 50                              | $6^{(*)3}$                           | 3                 |
| Comparative Example | 2 Current density : $50 \text{ A/m}^2$            | 25V  | 0.83                   | 100                             | $\geq 3^{(*)3}$                      | 3                 |
|                     | Ultimate voltage : 30 V                           |  |                        |                                 |                                      |                   |
|                     | Current controlled pretreatment prior to coloring |  |                        | 50                              | No coloring                          |                   |
|                     | 3 Current density : $50 \text{ A/m}^2$            | 14V  | 0.50                   | 100                             | No coloring                          |                   |
|                     | Ultimate voltage : 30 V                           |  |                        |                                 |                                      |                   |
|                     | Constant voltage pretreatment prior to coloring   |  |                        |                                 |                                      |                   |
| Comparative Example | 4 Bath voltage : 30 V                             | 21V  | 0.70                   | 100                             | $\geq 4^{(*)3}$                      | 4                 |
|                     | Treating time : 30 seconds                        |  |                        |                                 |                                      |                   |

(Notes) \*1) Peak voltage of alternating current during alternating current electrolytic coloring

\*2) Voltage ratio=peak voltage / ultimate voltage

\*3) Extremely large dependence on coloring time

### Industrial Applicability

According to this invention, it is possible not only to secure uniformity in color tone in a given energizing lot but also prevent irregular coloring in different energizing lots as much as possible in alternating current electrolytic coloring of aluminum materials and produce aluminum materials colored in a uniform tone commercially and stably.

What is claimed is:

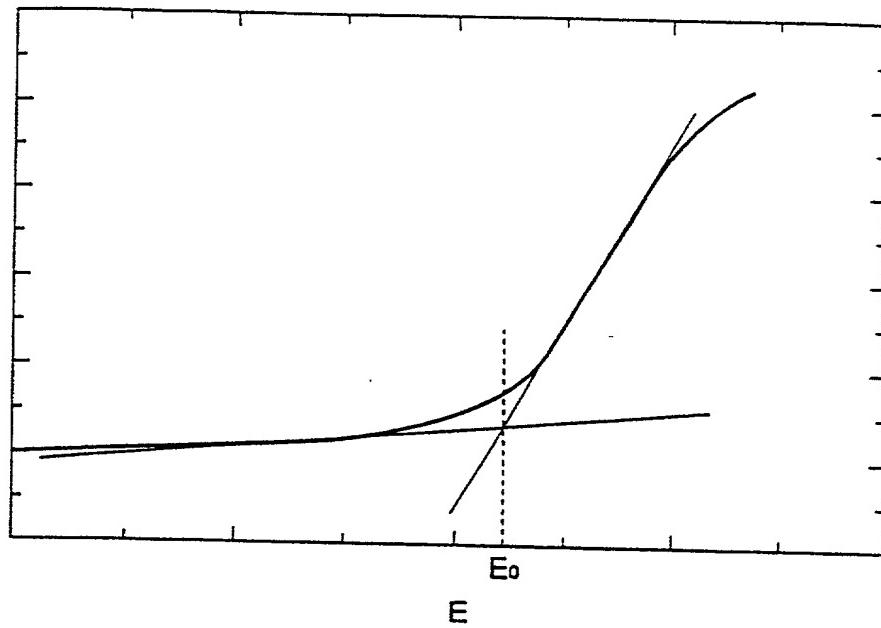
- (1) In a process for electrolytically coloring an aluminum material which comprises immersing an aluminum material consisting of anodized aluminum or an anodized aluminum alloy in an electrolytic coloring bath containing a soluble metal salt, performing a pretreatment prior to coloring by passing a direct current waveform with said aluminum material serving as the anode, and performing alternating current electrolytic coloring in the same electrolytic coloring bath, an improved process for electrolytically coloring an aluminum material which comprises performing said pretreatment prior to coloring until the voltage and current respectively reach the preset ultimate values.
- (2) A process for electrolytically coloring an aluminum material as described in claim 1 wherein said pretreatment prior to coloring is constant current electrolysis effected by passing a direct current waveform while maintaining the current at the preset ultimate value and the constant current electrolysis is continued until the voltage reaches the preset ultimate value.
- (3) A process for electrolytically coloring an aluminum material as described in claim 2 wherein said alternating current electrolytic coloring is performed by passing to the aluminum material a voltage-controlled alternating current waveform having the peak voltage which is 0.55-0.8 times the final voltage in the pretreatment prior to coloring.
- (4) A process for electrolytically coloring an aluminum material as described in claim 1 wherein said pretreatment prior to coloring is constant voltage

electrolysis effected by starting the passage of a direct current waveform at a voltage lower than the preset ultimate value, then switching over to the ultimate value, and passing a direct current waveform and the constant voltage electrolysis is continued until the current reaches the preset ultimate value.

(5) A process for electrolytically coloring an aluminum material as described in any one of claims 1 to 4 wherein the aluminum material pretreated prior to coloring and placed in the electrolytic coloring bath is scanned by alternating current voltage to plot a voltage-current curve, the boundary voltage  $E_0$  is determined from the intersection of the respective extension lines of the flat and rising regions of the voltage-current curve, and the peak voltage in alternating current electrolytic coloring is controlled below the boundary voltage  $E_0$ .

Abstract

This invention relates to an improvement of a process for electrolytically coloring an aluminum material comprising immersing an aluminum material consisting of anodized aluminum or an anodized aluminum alloy in an electrolytic coloring bath containing a soluble metal salt, performing a pretreatment prior to coloring by passing a direct current waveform with said aluminum material serving as the anode, and performing alternating current electrolytic coloring in the same electrolytic coloring bath and the improved process comprises performing said pretreatment prior to coloring until the voltage and current respectively reach the preset ultimate values. It is possible to prevent as much as possible an occurrence of irregular coloring not only in one energizing lot but also in different energizing lots and produce an aluminum material colored in a uniform tone stably and readily on a commercial scale.



Docket No.



**RADER, FISHMAN & GRAUER, PLLC**

# Declaration For U.S. Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below). I declare under penalty of perjury that the foregoing is true and correct.

are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled  
**(Insert Title) Process For Electrolytically Coloring Aluminum Material**

the specification of which is attached hereto unless the following box is checked:

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate or PCT International Application having a filing date before that of the application(s) for which priority is claimed:

|                                   |                                |                           |   |   |
|-----------------------------------|--------------------------------|---------------------------|---|---|
| (List prior foreign applications) | <u>179563/1999</u><br>(Number) | <u>Japan</u><br>(Country) | <u>25/06/1999</u><br>(Day/Month/Year Filed) | Priority Claimed  |
|                                   | <u>179564/1999</u><br>(Number) | <u>Japan</u><br>(Country) | <u>25/06/1999</u><br>(Day/Month/Year Filed) | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
|                                   |                                |                           |   | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

See attached list for additional prior foreign or provisional applications.

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or §365(c) of any PCT International application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) (U.S. or PCT) in the manner provided by the first paragraph of 35, U.S.C. §121, I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(List prior U.S. Applications or PCT International applications designating the U.S.)

|                          |               |   |
|--------------------------|---------------|---|
| (Application Serial No.) | (Filing Date) | (Status) (patented, pending, abandoned) |
| (Application Serial No.) | (Filing Date) | (Status) (patented, pending, abandoned) |

And I hereby appoint the firm of Rader, Fishman & Grauer, PLLC, Customer Number 23353 including as principal attorneys: Richard D. Grauer, Reg. No. 22,388; David T. Nikaido, Reg. No. 22,663; Ronald P. Kananen, Reg. No. 24,104; H. Lawrence Smith, Reg. No. 24,900; Ralph T. Rader, Reg. No. 28,772; Carl Schaukowitch, Reg. No. 29,211; Michael D. Fishman, Reg. No. 31,951; Joseph V. Coppola, Sr., Reg. No. 33,373; Michael B. Stewart, Reg. No. 36,018; Alexander D. Rabinovich, Reg. No. 37,425; Kevin D. Rutherford, Reg. No. 40,412; Glenn E. Forbis, Reg. No. 40,610; Kristin L. Murphy, Reg. No. 41,212; Matthew J. Russo, Reg. No. 41,282; Robert S. Green, Reg. No. 41,800; David K. Benson, Reg. No. 42,314; Brian K. Dutton, Reg. No. 47,255; Eugene G. Byrd, Reg. No. 47,361

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The undersigned hereby authorizes the U.S. attorneys named herein to accept and follow instructions from the undersigned's assignee, if any, and/or, if the undersigned is not a resident of the United States, the undersigned's domestic attorney, patent attorney or patent agent, as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and the undersigned. In the event of a change in the person(s) from whom instructions may be taken, the U.S. attorneys named herein will be so notified by the undersigned.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

✓/W Full name of sole or first inventor

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Inventor's signature

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